

**VERSION WITH MARKINGS TO SHOW CHANGES MADE****In the Specification**

Paragraph beginning at page 1 line 6 has been amended as follows

Reforming [Reformation] reactions for materials such as methane may be carried in a dry reforming process or a steam reforming process and may use a fixed bed or a fluidized bed.

Steam reforming of methane is a process in which methane is brought into contact with steam at high temperature (1100 K) and pressure (3000 kPa) over a catalyst. The result is the production of a mixture of CO, CO<sub>2</sub> and H<sub>2</sub>, commonly referred to as synthesis gas or syngas. Steam reforming of methane is the major source of synthesis gas for the production of chemicals such as methanol and ammonia and is the primary source of syngas for hydrogen production. On the industrial scale, steam reforming of methane is carried out in fixed bed reactors using a catalyst composed of nickel dispersed on a monolithic support such as  $\alpha$ -alumina or magnesia see for example C. N., Satterfield, Heterogeneous Catalysis in Industrial Practice, McGraw Hill, Inc. New York, 1991. Steam to methane ratios in excess of 3:1 are used in order to promote high conversions of methane and limit the production of coke.

Paragraph beginning at page 3 line 11 has been amended as follows

F., Arena, B., Horrell, D., Cocke, A., Parmaliana, N., Giordano, "Magnesia-Supported Nickel Catalysts: I. Factors affecting the structure and Morphological Properties", Journal of Catalysis, vol132, pg. 58, 1991 and A., Parmaliana, F., Arena, F., Frusteri, S., Coluccia, L., Marchese, G., Martra, A., Chuvilin, "Magnesia-Supported Nickel Catalysts: II. Surface Properties and Reactivity in Methane Steam Reforming", Journal of Catalysis, vol141, pg. 34, 1993 reported on their investigations of the use of magnesia (MgO) as a catalyst. Even though this type of catalyst was found to be both active and stable, magnesia showed an important drawback: as calcination temperature increased, the amount of available [manganese] nickel was reduced. This was attributed to the presence of free magnesia in the support which, when hydrated, formed a non-reducible NiO-MgO solid phase.

Paragraph beginning at page 3 line 25 has been amended as follows

Faujasites have been shown to be effective in several catalytic applications. The basic building block of the faujasite is a truncated octahedron that is connected at four of the hexagonal faces by hexagonal prismatic structures of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. The three dimensional framework includes elliptically shaped cavities approximately 12 Å in diameter called super cages. The Y-type zeolites with high (1.5 - 3.0) Si/Al ratios, 300 to 800 m<sup>2</sup>/g surface areas, are preferred given the thermal stability and the high catalytic activity. [Is it] See C.V., McDaniel, P.K., Maher, "Zeolite stability and ultra stable zeolites", Zeolite Chemistry and Catalysis, vol 4, pg.225, 1984?]

Only a few studies of methane reforming have been conducted using nickel supported on zeolites see M., Iwamoto, T., Hasuwa, H., Furukawa, S., Kagawa, "Water Gas Shift Reaction Catalyzed by Metal Ion-exchanged Zeolites", Journal of Catalysis, vol79, pg. 291, 1983 and B., Gustafson, J., Lunsford, " The Catalytic Reaction of CO and H<sub>2</sub>O over Ruthenium in a Y-Type Zeolite", Journal of Catalysis, vol78, pg. 393, 1982. [16,17]. . These studies suggest that higher activity can be attained using zeolitic supports. In addition to higher activity, zeolitic supports have the potential to deliver very high metal dispersion that is stable combined with a low potential for support metal interaction.

The paragraph beginning at page 4 line 12 has been amended as follows

There are many patents on [catalysts that] catalysts that describe various catalyst structures for example US patent 4,280,820 issued July 28 1981 describes a catalyst for use in the production of methane producing gases. This catalyst is formed by coprecipitation of Nickel Ni and alumina with in its unreduced precursor with a 12 to 120 Angstrom pores ([□] Å) and has at least 55% of the pore volume in the 12 to 30 [□] Å range and wherein the pore volume formed by pores with a radius of 10 to 50 [□] Å is at least 80% of the total pore volume

The paragraph beginning at page 4 line 18 has been amended as follows

US patents 4,990,481 issued February 5 1991 and 5,100,857 issued March 31 1992 to Sato et al each describes a catalyst formed by immersing the alumina particles in a Ni containing solution, drying and then calcining to produce a catalyst where the alumina has a pore size in the order of about 1000[□] Å to 5000[□] Å. It will be noted that these patents do not describe the size of the Ni crystallites.

The paragraph beginning at page 5 line 11 has been amended as follows

It is a further object of this invention to provide a fluidizable catalyst for [an] improved fluidized bed reforming processes.

The paragraph beginning at page 5 line 13 has been amended as follows

It is yet another objective of the present invention to provide a fluidizable catalyst specially adapted for use in an improved methane [stream] steam reforming process.

The paragraph beginning at page 5 line 15 has been amended as follows

Broadly the present invention relates to a regeneratable Nickel (Ni) catalyst particularly suited for a hydrocarbon reforming process, said catalyst comprising discrete Ni crystallites formed on a suitable support element by a several incipient wetness steps process and capable of withstanding at least 6 catalyst regenerations without significantly inhibiting [it] it's catalytic activity in said reforming process, said Ni crystallites being position in the inner surface of said suitable support element said crystallites having an average maximum dimension measured in any one direction in the range of between 10 and 1000 [ $\square$ ]  $\text{\AA}$  and a distribution on said support element of no more than 0.2 of said square meter ( $\text{m}^2$ ) of exposed nickel/ square meter ( $\text{m}^2$ ) of support surface.

The paragraph beginning at page 5 line 26 has been amended as follows

Preferably, said support element comprises alumina and average size of said Ni cryatallites is in the range of between 150 [ $\square$ ]  $\text{\AA}$  and 250 [ $\square$ ]  $\text{\AA}$  and a distribution of said Ni crystallites on said support element of no more than 0.14  $\text{m}^2$  of nickel /  $\text{m}^2$  of said support with an average pore size between 1000[A]  $\text{\AA}$  to 10000 [A]  $\text{\AA}$ , and a specific surface area of less than 10  $\text{m}^2/\text{gram}$  (g) of catalyst.

The paragraph beginning at page 6 line 3 has been amended as follows

Preferably, said support element comprises alumina and said average pore size is in the range of between [ $\square$ ]2000 [ $\square$ ]  $\text{\AA}$  and 5000 [ $\square$ ]  $\text{\AA}$  and a distribution on said support element of no more than 2[ $\square$ ] of said  $\text{m}^2/\text{gram}$  (g) of catalyst.

The paragraph beginning at page 6 line 6 has been amended as follows

Preferably, said support element comprises zeolite and said average zeolite cage size is in the range of between 5 [□] Å and 100 [□] Å and a specific surface area of [ ] 1000 of said m<sup>2</sup>/g

The paragraph beginning at page 6 line 8 has been amended as follows

Preferably, said support element comprises zeolite and said average size is in the range of between 5 [□] Å and 20 [□] Å and a distribution on said support element of no more than 500 of said m<sup>2</sup>/g. Preferably, said zeolite is selected from the group consisting of sodium exchanged Y type zeolite (NaY) and ultrastabilized Y type zeolite (USY).

The paragraph beginning at page 6 line 12 has been amended as follows

Preferably, said support element has an average zeolite cage size in the range of between 11 [□] Å and 14 [□] Å.

The paragraph beginning at page 6 line 14 has been amended as follows

Preferably, said suitable support element has an average size in the range of between 12[□] Å and 13 [□] Å.

The paragraph beginning at page 6 line 16 has been amended as follows

Broadly the present invention also relates to a reforming process comprising reforming hydrocarbons in the presence of a catalyst in a reaction zone, said catalyst being Nickel (Ni) catalyst of discrete Ni crystallites formed on said support by a several step incipient wetness process, said crystallites having an average size measured in any one direction in the range of between 10 and 1000 [□] Å and a distribution on said support element of no more than 0.2 of said square meter of nickel exposed metal/ square meter of support selected from alumina and zeolite materials recycling said catalyst to and from said reaction zone, regenerating between 10 and 100 % of the catalyst being recycled in a regeneration zone to provide a regenerated catalyst and returning said regenerated catalyst to said reaction zone

The paragraph beginning at page 8 line 1 has been amended as follows

The reactor 10 has an upper primary section 24 and a lower secondary section 26. Sweep gas is introduced at the bottom of the [ractor] reactor 10 i.e. into the secondary section 26 as indicated by the arrows 28. Hydrogen gas leaves the reactor 10 adjacent to the top of the secondary stage as indicated by line 30. The synthetic gas produced in the reactor 10 plus some coked catalyst

leave via line 32 and are separated in the cyclone separator 34 with the synthetic gas being available from line 36 and the coked catalyst being returned via line 38 some of which is recirculated via line 20 and the remainder of which passes via line 40 to the regenerator 42 where it is oxidized via oxygen or air introduced as indicated at 44. Gases are separated from the decoked catalyst in separator 46 and the decoked catalyst returned via line 18 as above described.

The paragraph beginning at page 8 line 13 has been amended as follows

The dry reforming process or CO<sub>2</sub> reforming shown in Figure 2 is similar to that of Figure 1, however the line 16 introducing [stream] steam in figure 1 is replaced by a line 16A introducing carbon dioxide (CO<sub>2</sub>) in place of the steam. The remainder of the process is quite similar to the steam process of Figure 1.

The paragraph beginning at page 8 line 23 has been amended as follows

With the above factors in mind, Nickel (Ni) was chosen to be used as the active metal as it will provide suitable activity, be cost effective and aid in the ease of comparison between the proposed process and current industrial practice.

The paragraph beginning at page 9 line 1 has been amended as follows

Support structures may be made of a number of conventionally used suitable support materials, however it has been found that alumina or zeolite materials are particularly effective and thus suitable supports will generally have similar physical characteristics to the alumina or zeolite materials preferred for this invention. Supports made from alumina, preferably [□] α-alumina have been found to be effective for both the steam reforming processes the dry reforming processes. Zeolite support structure are not particularly suited to steam reforming as the high pressure steam used in this process has been found to be detrimental to the zeolites, but zeolite support structures particularly NaY (sodium exchanged Y type zeolite) and USY (ultrastabilized Y type zeolite]support structures have been found to be very effective in a dry reforming process).

The paragraph beginning at page 9 line 16 has been amended as follows

Figure 3 is an example of a catalyst constructed according to the invention. As shown the catalyst 100 includes a support 102 has a major dimension L which may range in size from 5 to

200 microns and is formed with a network of internal pores 104. A plurality of catalyst material crystallites (Ni crystallites) 106 are [position] positioned in spaced apart relationship with the minimum space between adjacent crystallite or maximum nickel surface coverage of 0.2 square meters ( $m^2$ ) of exposed nickel/square meter ( $m^2$ ) of support. The crystallites have a characteristic dimension as indicated at "l". This dimension "l" will be discussed in more detail below.

The paragraph beginning at page 9 line 24 has been amended as follows:

It has been found that the size range characteristic dimension "l" for the Ni crystallites should be in the range of 10 [ ] Å to 1000 [ ] Å and preferably are in the range of 150 to 250 [ ] Å.

These crystallites 104 are distributed on the support 100 so that there are no more than 0.2  $m^2$  of exposed nickel/  $m^2$  of support i.e. a minimum spacing between adjacent crystallites or maximum coverage of the surface support.

The paragraph beginning at page 10 line 1 has been amended as follows:

The average range of size i.e. dimension l of the crystallites 104 when [ ]  $\alpha$ -alumina (the preferred form of support for steam reforming) is used as the support structure will generally be in the range of 10[ ] Å to 1000[ ] Å preferably 150[ ] Å to 250[ ] Å and for zeolite supports will normally be smaller than those for  $\alpha$  alumina and generally will be in the range of 5[ ] Å to 100[ ] Å preferably 30[ ] Å to 70[ ] Å. It has been found that when the size and distribution of Ni crystallites are not within these ranges the resulting product has catalyst properties significantly inferior to those of the present invention.

The paragraph beginning at page 10 line 8 has been amended as follows:

Attention is directed to Figure 6 which shows the relationship of crystallite size in [ ] Å versus exposed Ni surface/ unit of support area. It is very clear that the maximum ratio is obtained at a crystallite size of about 250 to about 350 [ ] Å.

The paragraph beginning at page 10 line 13 has been amended as follows:

The catalyst is particularly suited for fluidized bed use as it may be provided in the form of fluidizable catalyst crystallites having a size L of between 5[ ] and 200 microns and [ ]

preferably between 20 to 100 microns. and an apparent density in the range of [ ]0.5[ ] to 2 [Kg/m<sup>3</sup> ] Kg/m<sup>3</sup> preferably of 0.7 [ ] to 1.3 [Kg/m<sup>3</sup> ] Kg/m<sup>3</sup>.

The paragraph beginning at page 10 line 23 has been amended as follows

It is clear that to practice the present invention and provide a catalyst with the required crystallite properties care must be taken in the manufacture of the catalyst to ensure the desired small crystallite size of the Ni is obtained. It has been found that to provide crystallites having the required characteristics it is essential [the] they be formed on the support by a multi [stage] step incipient wetness process as will be described in more detail below.

The paragraph beginning at page 11 line 13 has been amended as follows

After impregnation the catalyst was heated at a rate of 0.5°C to 140°C and allowed to dry for 6 hours. Once the solution evaporated the crystals [Ni(NO<sub>3</sub>)<sub>2</sub>] Ni(NO<sub>3</sub>)<sub>2</sub> were formed and deposited in the inner surface of the catalyst. Following this the catalyst was placed in a fluidized bed reactor located in a vertical tube furnace and fluidized with a 10% hydrogen 90 % helium gas mixture. Over four hours, the temperature of the bed was raised from ambient to 450°C and held there for two additional hours. This treatment had the effect of thermally decomposing the monoclinic crystals of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into the cubic crystals of NiO and HNO<sub>3</sub> and reducing the NiO produced to cubic Ni<sup>0</sup> crystals

The paragraph beginning at page 11 line 21 has been amended as follows

The number of impregnation/thermal decomposition cycles, required to reach the desired crystal size and metal dispersion (area of exposed nickel over the area of support) , was determined by the extent of metals dispersion that could be reached in one impregnation. This in turn was dictated by the incipient wetness properties of the support. Typically, four cycles were required to reach a 0.14 m<sup>2</sup> of exposed nickel /m<sup>2</sup> of support having crystallite size of nickel of about 170 [A] Å average size on α-alumina.

The paragraph beginning at page 13 line 7 has been amended as follows

Catalyst activity was assessed in a bench scale unit specifically designed for the simulation of fast fluidization (riser or downer operation) called the CREC Riser Simulator which is d scribed

in more detail in US patent 5,102,628 the disclosure of which is incorporated herein by reference. Reactions in the Riser Simulator are carried out in a batch fashion by injecting the reactants, actively mixing the reactor and then terminating the reaction by venting the contents to a sample bottle see K., Jarosch, H.I., de Lasa, "Novel Riser Simulator for Methane Reforming using High Temperature Membranes", Chem. Eng. Sci., vol54, pg. 1455, 1999 for further information. Catalyst activity was assessed for measuring steam reforming by measuring the conversion of methane at fixed contact times (30 and [60s] 60 seconds (s)) under standard conditions (750°C, Steam/methane ratio~2.3, C/O = 6.0, Total Pressure 2200 kPa).

The paragraph beginning at page 13 line 18 has been amended as follows

The nickel crystallites were smaller for USY and NaY zeolites, 60 [□] Å and 40 [□] Å respectively over the crystallites on α-alumina (179 [□] Å) and for this reason it was anticipated that the zeolite-based catalysts would be more active than the α-alumina catalysts. However, when the conversion of methane at 60 [s] seconds (s) was compared, the α-alumina based catalyst was found to be more active. A methane conversion of 51%, close to the equilibrium conversion, was observed over the α-alumina while the conversion of methane observed over the NaY zeolite was only 35%.

The paragraph beginning at page 13 line 25 has been amended as follows

Furthermore, when the activity assessment was repeated it was found that over a time-on-[steam] stream of 360 s, the activity of the NaY zeolite based catalyst declined dramatically, falling from 35% to 13%, while that of the α-alumina remained relatively stable. A similar loss of activity was noted over nickel/USY catalysts. The loss of activity observed over the Y-type zeolites was found to be due to the high steam partial pressures used (>1700 kPa) [7]. Therefore, although useful for the production of high and stable metal dispersions, Y-type zeolites were found unsuitable for the steam reforming of methane. However, nickel supported on zeolites can be, as described later, [be] very valuable catalysts for dry methane reforming (methane reforming with CO<sub>2</sub>) as reforming takes place in an atmosphere that is essentially steam free, thus preserving the structure of the zeolites.

The paragraph beginning at page 14 line 8 has been amended as follows



Having established that the Y-type zeolites were unsuitable for use in the steam-reforming version of the *Catformer*, attention was focused on the nickel  $\alpha$ -alumina catalyst. Experiments were conducted using  $\alpha$ -alumina impregnated with 179 [□] Å average size crystallites and 0.14 m<sup>2</sup> exposed nickel /m<sup>2</sup> of support, 529 [□] Å average size crystallites and 0.058 m<sup>2</sup> of exposed nickel/m<sup>2</sup> of support and 1929[□] Å average and 0.04 m<sup>2</sup> of exposed nickel/m<sup>2</sup> of support in order to determine the effect of crystallite sizes and time-on-stream on activity (Figure 5). In this case, the activity was measured as the conversion of methane after a 30 s contact time as conversions close to equilibrium were observed after 60 s over 1929[□] Å average size crystallites and 0.04 m<sup>2</sup> of exposed nickel /m<sup>2</sup> of support on  $\alpha$ -alumina catalyst.

The paragraph beginning at page 14 line 18 has been amended as follows

As previously mentioned, 179[□] Å average size crystallites and 0.14 m<sup>2</sup> exposed nickel /m<sup>2</sup> of support, 529 [□] Å average size crystallites and 0.058 m<sup>2</sup> of exposed [nickel/m<sup>2</sup>] nickel/m<sup>2</sup> of support and 1929[□] Å average and 0.04 m<sup>2</sup> of exposed nickel/m<sup>2</sup> of support nickel encompassed the low and high values of metal loading on conventional reforming catalysts, and it was felt that these catalysts would bracket the optimal metal loading level. However, when the activity of these two loadings were compared, 39.5±3.7% for the 179[□] Å nickel crystallites and 38.9±2.3% for the 529[□] Å nickel crystallites it was found that the difference in activity was not statistically significant. When the metal loading was decreased to 179[□] Å nickel crystallites , the activity increased and the conversion of methane was found to be 46.9±4.0%. Further reduction of the metal loading level led to a sharp drop in catalyst activity. These results are shown in Figure 4 in which the broken line represents the methane equilibrium conversion [form] for thermodynamic calculations. In generating this plot the contact time in Riser Simulator = 30 s, Catalyst cycle = First, Temperature = 750 °C, H<sub>2</sub>O/ Methane = 2.2, Pressure = 2.2 MPa EI.

The paragraph beginning at page 15 line 3 has been amended as follows

Further results showing the effectiveness of the Ni [□]  $\alpha$ -alumina for the present invention over time have been plotted in Figure 5. Similar result are shown for USY zeolites in Figure 8

The table 2 beginning at page 16 line 1 and the line immediately therebelow have been amended as follows

**Table 2. Changes of Ni dispersion on the support with oxidation- reduction cycles.**

Ni Crystallite size	Run 4	Run 5	Run6
179[□]Å	0.14	0.167	0.136
529[□]Å	0.058	0.068	0.0443
1929[□]Å	0.04	0.049	0.0277

[Table 3]

Table 3 summarizes the results of the BET tests for nickel catalyst supported on both  $\alpha$ -

The paragraph beginning at page 19 line 8 has been amended as follows

The reactivity results obtained with the Ni-zeolite fluidizable catalysts of the present invention in the CREC Riser Simulator were very successful (Figure 8). It was shown that at 600KPa, 750-800°C, 10-15 [s] seconds reaction time, a 60% methane conversion could be reached for a 0.33 to 2 CH<sub>4</sub>/CO<sub>2</sub> ratio and all this with low coke selectivity.

#### **In the claims**

Claim 1 has been amended as follows

1. A regenerable Nickel (Ni) catalyst particularly suited for a hydrocarbon reforming process, said catalyst comprising discrete Ni crystallites formed on a suitable support element by a several incipient wetness steps process and capable of withstanding at least 6 catalyst regenerations without significantly inhibiting [it] it's catalytic activity in said reforming process, said Ni crystallites being [position] positioned in the inner surface of said suitable support element said crystallites having a crystallite characteristic dimension measured in any one direction in the range of between 10 and 1000 [□] Å and a distribution on said support element of no more than 0.2 square meter of exposed nickel/square meter of support surface.

Claim 4 has been amended as follows

4. A catalyst as defined in claim 3 wherein said crystallite characteristic dimension measured in any one direction in the range of between 10 and [1000\_□] 1000Å average size and a distribution on said support element of no more than 0.2m<sup>2</sup> of exposed nickel /m<sup>2</sup> of said support surface.

Claim 5 has been amended as follows

5. A catalyst as defined in claim 3 wherein said average size is in the range of between 150 [□] Å and 250 [□] Å and a distribution on said support element of no more than 0.16 of said m<sup>2</sup> of exposed nickel / m<sup>2</sup> of said support surface.

Claim 9 has been amended as follows

- 9 A catalyst as defined in claim 8 wherein said average size is in the range of between 5 [□] Å and 100 [□] Å and a distribution on said support element of no more than 0.15 m<sup>2</sup> nickel exposed / m<sup>2</sup> of said support surface.

Claim 10 has been amended as follows

- 10 catalyst as defined in claim 8 wherein said average size is in the range of between 10 [□] Å and 70 [□] Å of no more than 0.10 m<sup>2</sup> nickel exposed / m<sup>2</sup> of said support surface.

Claim 23 has been amended as follows

- 23 A reforming process comprising reforming hydrocarbons in the presence of a catalyst in a reaction zone, said catalyst being Nickel (Ni) catalyst of discrete Ni crystallites formed on said support by a several step incipient wetness process, said crystallites having a maximum dimension measures in any one direction in the range of between 10 and 1000 [□] Å and a distribution on said support element of no more than 0.2 of said square meter of nickel exposed metal/ square meter of support selected from alumina and zeolite materials recycling said catalyst to and from said reaction zone, regenerating between 10 and 100 % of the catalyst being recycled in a regeneration zone to provide a regenerated catalyst and returning said regenerated catalyst to said reaction zone

**In the Abstract**

The abstract has been amended as follows

A Nickel (Ni) catalyst for facilitating a hydrocarbon reforming process, and an improved process based on the catalyst. The catalyst comprising discrete Ni crystallites having a size in the range of between 150 and 250 [□] Å and a distribution on said support element of no more than 0.14 square meters of exposed nickel/square meter of support